



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/NL96/00087</p> <p>(22) International Filing Date: 22 February 1996 (22.02.96)</p> <p>(30) Priority Data: 95200440.6 22 February 1995 (22.02.95) EP (34) Countries for which the regional or international application was filed: AT et al.</p> <p>(71) Applicant (for all designated States except US): ELF ATOCHEM VLISSINGEN B.V. [NL/NL]; Haven 9850, Vlissingen-Oost, NL-4380 AB Vlissingen (NL).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): HOEKMAN, Leendert, Cornelis [NL/NL]; Kamperfoeliestraat 44, NL-4461 NM Goes (NL). CARSON, Stephen, W. [US/US]; 1620 Russel Drive, Downingtown, PA 19335 (US).</p> <p>(74) Agent: SMULDERS, Th., A., H., J.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: PROCESS FOR PRODUCING A PROTECTING COATING ON A SURFACE OF A GLASS OR CERAMIC ARTICLE</p> <p>(57) Abstract</p> <p>The invention relates to a process for producing a protecting coating on a surface of a glass or ceramic article, said coating having an improved resistance to caustic wash treatments. In carrying out the inventive process a stream of an oxygeneous carrier gas containing a thermodecomposable precursor of tin oxide (SnO<sub>2</sub>) and a thermodecomposable precursor of silicon oxide (SiO<sub>2</sub>) in a molar ratio of the former precursor to the latter between 0.6 and 3.0, said precursors being present in evaporated form, and further containing water vapor in an amount of at least 1 mole per 100 moles of carrier gas, is uniformly impinged onto the surface to be coated, said surface having a temperature which is above the decomposition temperatures of said precursors and amounts to at least 550 °C, to deposit a mixed oxide protecting coating comprising tin oxide and silicon oxide, and the deposition is continued until a coating thickness of between 240 and 1,500 Å is obtained.</p>		

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Title: Process for producing a protecting coating on a surface of a glass or ceramic article.

The invention relates to surface coating glass or ceramic articles, in particular glass containers such as bottles, which are intended for repeated use after having been washed with a caustic solution.

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It is known to treat the surface of glass articles in order to improve the abrasion resistance. For instance, US-A-4 144 362 describes the coating of glass bottles with a thin film of tin oxide. The tin oxide coatings are obtained by exposing the glass surface, heated at a temperature between 450°C and 600°C, in an oxygeneous atmosphere, e.g. in air, to an organic tin compound in vapor form or in finely divided form. In contact with the hot glass surface the tin compound is decomposed and oxidized to form a coating of tin oxide. The coating technique described and illustrated in US-A-4 144 362 results in the production of tin oxide coatings having a thickness in the order of 45-120 Å.

According to US-A-4 130 673 a thin layer of a natural wax or a synthetic polymer is applied on top of a tin oxide surface coating produced as described above after the tin oxide coated article has been cooled to a temperature of 350°C or less. The combination of the two coating layers is said to reduce scratching and breaking of the glass articles during handling and processing.

There is an increasing trend of using glass containers, e.g. glass bottles, over and over again. Before the containers can be refilled they are subjected to a heavy wash treatment, using e.g. caustic solutions. After 5-15 wash cycles at 80°C using caustic solutions at 1-4%, a tin oxide coating which has been produced as described above will be completely removed.

First, after a few wash cycles, thick spots of the tin oxide coating get an unacceptable strong bluish color. On subsequent wash cycles the coating shows greyish spots and finally disappears.

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EP-A-0 485 646 aims at producing refillable glass bottles which are provided with a metal oxide coating which would resist an eight-hour treatment with a 4% caustic solution at 80°C. The coating comprises tin oxide or titanium oxide and  
10 has a thickness of 400 to 1,000 Å. The coating is made by contacting a tin compound such as tin tetrachloride or dimethyl tin dichloride or a titanium compound such as titanium tetrachloride with a glass bottle which has an external surface temperature of 550 to 700°C.

15

The thicker tin oxide coatings prepared according to EP-A-0 485 646 provide a better protection against caustic wash than the thinner coatings known from the US patents discussed above. However, tests which have been carried out by the  
20 present inventors show that these thicker coatings become rather hazy after 2 to 6 hours of washing (using a 4% caustic solution at 80°C), making the bottles less acceptable for long lasting repeated use. As far as titanium oxide coatings are concerned, it can be observed that the titanium starting  
25 compound is hard and difficult to handle and is very inefficient in use.

WO 93/13393 discloses a process for coating glass by chemical vapor deposition (CVD) using a composition comprising a  
30 mixture of a tin oxide precursor, a silicon oxide precursor and an accelerant, preferably triethyl phosphite. The composition is deposited at a rate greater than about 350 Å/sec to form a coating which according to the Examples has a thickness between 2,000 and 4,930 Å. The coating thus  
35 obtained can be combined with other layers to produce an article with specific properties such as controlled emissivity, refractive index, abrasion resistance or

appearance. In Example 7 a clear glass bottle is coated with a vapor mixture comprising a tin oxide precursor, a silicon oxide precursor, triethyl phosphite and hot air, the molar ratio of the tin oxide precursor to the silicon oxide precursor being 0.2. The vapor mixture is deposited for 10 seconds at an estimated deposition rate of about 200 Å/second to produce a magenta-blue colored film having a thickness of about 2,000 Å. Without the presence of triethyl phosphite the deposition rate is about 50 Å/second.

10

The present invention provides a process for producing a protecting coating for glass or ceramic articles, said coating being highly resistant to caustic wash treatments.

15 The process of the present invention also provides an improved coating for glass containers, said coating remaining clear and substantially unchanged when the glass container is subjected many times to caustic wash treatments preparatory to a next use thereof.

20

According to a further object of the present invention a wax coating is applied on top of the protecting coating, thus making the glass or ceramic articles better resistant to scratches.

25

The present invention also provides a simple, efficient and reliable process for producing an improved protecting coating on a surface of a glass or ceramic article, wherein thermodecomposable precursors are used which are easy to handle.

30

In producing a protecting coating on a surface of a glass or ceramic article according to the present invention, a stream of an oxygeneous carrier gas containing a thermodecomposable precursor of tin oxide ( $\text{SnO}_2$ ) and a thermodecomposable precursor of silicon oxide ( $\text{SiO}_2$ ) in a molar ratio of the former precursor to the latter between 0.6 and 3.0, said

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precursors being present in evaporated form, and further containing water vapor in an amount of at least 1 mole per 100 moles of carrier gas, is uniformly impinged onto the surface to be coated, said surface having a temperature which is above the decomposition temperatures of said precursors and amounts to at least 550°C, to deposit a mixed oxide protecting coating comprising tin oxide and silicon oxide, and the deposition is continued until a coating thickness of between 240 and 1,500 Å is obtained.

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CTU (coating thickness unit) is an optical unit which is frequently used in the glass industry for defining the thickness of coatings and is based on measurements of the reflection of incident light. For an oxide coating according to the invention a thickness of 1 CTU may be estimated to correspond with about 3 Å. For practical reasons and in accordance with what is usual in the art, the CTU thickness units will generally be adopted throughout the description and the Examples to follow.

20

When a protective coating produced according to the invention is compared with a known coating having the same CTU thickness, the inventive coating strikingly shows a considerably improved resistance to caustic wash treatments, while the coating maintains its clear appearance. The excellent properties which have been established, e.g. a good resistance to 50 and even more wash cycles of 8 to 10 minutes, make the inventive coating also very suitable for protecting ceramic articles such as crockery. Further, after a usual wax coating has been applied on top of the inventive coating, an excellent scratch resistance is obtained.

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Possible explanations for the excellent properties of the protecting coating produced according to the invention could be that the silicon oxide produced in the coating and the silicon oxide contained in the substrate to be coated, at least in part, melt together at the interface, and/or that the

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co-presence of silicon oxide results in a more tight coating or film having almost no openings through which caustic attack can take place, and/or that the co-presence of silicon oxide increases the resistance of the coating layer to the

5 mechanical impact on contact with cutlery or occurring in washing equipment. At present, the mechanism(s) causing the improvement is (are) not yet understood and therefore, the possible explanations detailed above have to be considered as hypothetical only and it is not intended to be bound by them.

10 The present process for producing a protective coating comprising tin oxide and silicon oxide is preferably carried out at the hot end of the production line for producing the glass or ceramic article, while the surface of the article is  
15 still hot enough for the precursor to be decomposed. Moreover, a surface temperature of at least 550°C is essential for producing a coating having the desired good properties. The production of the protecting coating by decomposition and oxidation of the precursors can be carried out by means of the  
20 CVD (Chemical Vapor Deposition) method comprising bringing the precursors in vapor form in contact with the hot surface to be coated.

25 According to the CVD method the precursors are applied from a stream of a carrier gas, conveniently air, impinging onto the surface to be coated and containing the precursors in evaporated form. For short deposition times, e.g. less than about 10 seconds, the deposition rate is proportional to the deposition time. However, when longer deposition times are  
30 applied the temperature of the surface will decrease resulting in a corresponding decrease of the deposition rate and of the efficiency of the coating process. Therefore, depending on the desired coating thickness, it can be necessary either to start the coating at a rather high surface temperature or to supply  
35 additional heat to the surface to be coated during the coating itself. A rather high temperature of the surface to be coated

is also advantageous for other reasons as will be discussed below.

The tin compound for use as a precursor according to the invention can be any tin compound which is capable of being thermally decomposed at the temperature of the surface of the glass or ceramic article to be coated. During decomposition reaction with oxygen present in the carrier gas results in the deposition of tin oxide. Suitable thermodecomposable tin compounds can be selected from monoalkyl tin trichlorides such as monomethyl tin trichloride and monobutyl tin trichloride, monoalkyl tin tribromides, dialkyl tin dichlorides such as dimethyl tin dichloride, dialkyl tin dibromides, and tin tetrachloride. Monobutyl tin trichloride is most preferred for use as precursor of tin oxide, because it is easy to handle and very efficient in use.

The silicon compound for use as a precursor should also be capable of being thermally decomposed and then producing silicon oxide as described above with respect to the tin compounds. Suitable silicon compounds are compounds having the formula  $R_nSiX_{(4-n)}$ , wherein R is an alkyl, an alkenyl, an alkynyl or an alkoxy group having 1-5 carbon atoms, or a phenyl group; X is a halogen atom or a hydroxy group; and n is a number from 0 to 4. Tetramethoxy silane, tetraethoxy silane and tetrapropoxy silane are examples of suitable silicon compounds.

The tin compound is preferably present in an amount of  $0.5 \times 10^{-4}$  -  $2 \times 10^{-2}$  mole per 1 mole of carrier gas. The molar ratio of the tin compound to the silicon compound is chosen between 0.6 and 3.0 in view of the high caustic wash resistance aimed at. There has been established that, within the indicated range, the best results are obtained when said molar ratio is at most 2.0 and preferably at most 1.5. It is further essential that the carrier gas, preferably air as said before, contains water vapor, which is present in an



amount of 1-50 mole(s) per 100 moles of the carrier gas. A sufficient amount of water vapor is usually contained in the air employed as the oxygeneous carrier gas when producing the inventive protecting coating by atmospheric-pressure CVD according to a preferred embodiment. It is evident that the carrier gas is at a temperature at which the precursors are in evaporated form. In general the temperature of the carrier gas is between 100°C and 210°C and a preferred temperature range is between 120°C and 180°C. The velocity at which the gas stream containing the components detailed above impinges onto the surface to be coated is usually selected in the range of 1-10 m/s and most preferably in the range of 3-5 m/s.

It is essential that the temperature of the glass or ceramic surface to be coated is above the decomposition temperature of the precursors used, but evidently below the softening temperature of the article to be coated. Usually, the protecting coating is applied at the hot end of the production line of e.g. glass bottles. A rather high temperature of the surface to be coated not only increases the deposition rate, as has been discussed before, but has also been found to substantially improve the resistance of the coated surface, in particular to caustic wash. Therefore, the temperature at the surface of the article should be at least 550°C during the coating process, the preferred temperature being at least 570°C and the most preferred temperature being at least 600°C, such as between 600°C and 650°C. Additional heat can be supplied to the article during the coating process in order to keep the surface temperature at the desired high value. Any suitable means for supplying additional heat is convenient such as flame projection etc.

The coating treatment is continued until the desired coating thickness is obtained. As a matter of fact, the coating thickness, in combination with the molar ratio of the tin compound to the silicon compound and a sufficiently high coating temperature as discussed above, provides the excellent

resistance to caustic wash, while the coating maintains a clear appearance. According to the invention the thickness of the protecting coating should be at least 80 CTU. At thicknesses of at least 150 CTU and preferably of at least 180 CTU the coatings have been found to withstand heavy wash treatments of 12 hours with 4% caustic solutions at 80°C without showing any haze or unwanted colors provided the temperature of the surface to be coated has been sufficiently high. Preferably the coating thickness is between 150 CTU (450 Å) and 900 Å.

In the Examples hereinbelow, given by way of illustration only, the compounds of tin and of silicon are introduced into a hot air stream by means of syringes in order to evaporate these compounds. The temperature of the air is about 150°C. The gas mixture is directed towards the surface of the glass articles to be treated by means of a tube, as is well known. In the examples, the opening of the tube is 15 x 35 mm. Glass bottles of 50 ml are treated over two-thirds of their height. They are heated in an oven to the desired temperature. The temperature is measured by means of a thermocouple disposed inside the bottles. The bottles are fixed by any appropriate means, for instance by means of a stick allowing the bottles to be handled and rotated during their exposure in the treatment gas stream. The temperature of the glass at the start of the formation of the coating is measured by means of an infrared thermometer (type CHINO IR-AHOT/-50°C to + 1000°C) set at an emissivity of 0.93, sensitive over a wavelength range of from 4 to 13 µm.

#### Test for measuring scratch resistance

Two bottles having had the same treatment are placed in horizontal position, one on top of the other, and they are pressed against each other, while causing them to slide over each other. When the pressure is increased, the moment of the scratch formation is clearly the moment when it is necessary to increase the force applied in order that the bottles

continue to slide over each other. The force of application is limited to 450 N as a higher force would lead to one or both bottles being crushed. Bottles having a suitable coating withstand a force of 450 N without sustaining scratches.

5

Test for measuring resistance to washing with a caustic solution

The test conditions correspond with those of bottle filling stations.

- 10 The bottles are immersed in a 4% sodium hydroxide solution maintained at 80°C. During the test, the container holding the caustic solution has to be purged with nitrogen to avoid any conversion of sodium hydroxide to sodium carbonate as a result of the presence of carbon dioxide present in the ambient air.
- 15 For the same reason, for each test a freshly prepared sodium hydroxide solution is used as sodium carbonate would cause less damage to the coating.

- For the test, 2-liter borosilicate glass containers of 150 mm diameter are used. These containers can contain 4 bottles. The
- 20 bottles are placed on a plate disposed 20 mm from the bottom of the container. Each bottle is retained by three pins of 6 mm diameter and 15 mm length, which are fixed in holes in the plate. The plate, in the middle thereof, has a hole of 30 mm diameter and 8 holes of 15 mm along its periphery.

- 25 The caustic solution is stirred using a stirrer of 40 mm length and 10 mm diameter, driven at 500 rpm by a magnetic stirring heating plate.

- The thickness of the coating is measured, using the device of the American Glass Research Co. (AGR). This device, commonly
- 30 used in the industry of bottle manufacture, measures the reflection of the treated glass surface, the reflection value being then converted to CTU's (Coating Thickness Units). 1 CTU for a mixed tin oxide/silicon oxide coating according to the invention obtained by the CVD method as described hereinabove,
- 35 corresponds to about 3 Å.

The following non-limiting examples illustrate the invention.

Examples 1 and 2 are comparative examples.

In Example 1, bottles are covered with a tin oxide coating and with a wax coating according to the teaching of U.S. Patent 4,130,673.

- 5 In Example 2, bottles are treated to provide them with a thicker tin oxide coating. To avoid an unacceptable haze, these coatings were formed utilizing higher tin compound concentrations and higher carrier gas velocities.

10 Example 1 (comparative)

Utilizing the procedure described above, a tin oxide coating is deposited on 4 bottles, starting from monobutyl tin trichloride. To this end, there is impinged on the surface of the glass bottles brought to a temperature of 600°C, a gas  
15 mixture comprising air as carrier gas, the tin compound in a ratio of  $1.5 \times 10^{-4}$  mole per mole of air and water vapor in a concentration of 2.3 moles per 100 moles of air. The air velocity is 3 m/sec. The deposition is effected in 2.5 sec. A tin oxide coating having a thickness of about 35 CTU is  
20 obtained.

Two of these bottles are then treated to be covered with a wax coating through pulverization of an aqueous suspension of poly(ethylene oxide) according to the process described in U.S. Patent 4,130,673. These two bottles show an excellent  
25 resistance to scratching at 450 Newtons. The bottles coated as described in each of the Examples hereinbelow show the same excellent resistance to the scratching after they have been covered in the same manner with a wax coating.

The two other bottles undergo the severe washing test in a  
30 caustic 4% solution at 80°C. The tin oxide coating is very much damaged after 15 minutes of washing and was completely removed after 30 minutes of washing.

Example 2 (comparative)

- 35 The general coating procedure described in Example 1 is utilized, including the temperature of 600°C at the surface of the glass bottles. Tin oxide coatings having thicknesses of

100 CTU, 150 CTU and 200 CTU were formed, starting from a gas mixture containing monobutyl tin trichloride in a ratio of  $1 \times 10^{-3}$  mole per mole of air and water vapor in a concentration of 2.3 moles per 100 moles of air. The air velocity is 5 m/sec. The deposition periods are, respectively, 3 seconds, 4.5 seconds, and 6 seconds.

The thickness of these coatings is higher than that of the coating of Example 1. Yet, after one hour of washing under the conditions of Example 1, all the tin oxide films are damaged and partly removed.

### Example 3

The general coating procedure described in Example 1 is utilized, including the temperature of 600°C at the surface of the glass bottles. In this example, bottles having two different coating thicknesses are prepared. The gas mixture used for forming the coatings on the bottles comprises monobutyl tin trichloride in a ratio of  $1 \times 10^{-3}$  moles per 1 mole of air, tetraethoxy silane in a ratio of 50 mole % of the mixture of the two metallic compounds, and water vapor in a concentration of 2.3 moles per 100 moles of air. The air velocity is 5m/sec. The deposition periods are, respectively, 4.5 seconds and 6 seconds.

The coatings obtained have thicknesses of 150 CTU and 200 CTU. They do not show any haze. As regards the resistance to washing with a caustic solution as realized in the conditions of the preceding Examples, after 12 hours of washing the coating having a thickness of 150 CTU shows only a slight haze and the coating of 200 CTU does not show any damage.

### Example 4

Coatings are formed on bottles as in Example 3, but tetrapropoxy silane is used instead of tetraethoxy silane. Similar results as in Example 3 are obtained.

Example 5

Coatings of a thickness of 150 CTU are formed as described in Example 3. However, the water vapor concentration in the gas mixtures used is varied. These concentrations are, respectively, 8 moles and 14 moles per 100 moles of air. All the coatings obtained show a similar excellent resistance to washing with caustic solution as that of the coating of 200 CTU of Example 3.

10 Example 6

The procedure is as in Example 3, except that instead of monobutyl tin trichloride, tin tetrachloride or monomethyl tin trichloride is used. In both cases, similar results as those of Example 3 are obtained.

15

Example 7

The procedure is as in Example 3, except that different temperatures of the surface of the glass bottles are used: viz 575°C and 625°C. Since at these high temperatures the deposition rates are about the same the deposition periods are, respectively, 4.5 seconds for a coating thickness of 150 CTU and 6 seconds for a coating thickness of 200 CTU. For both coatings thicknesses the resistance to washing with the caustic solution is quite acceptable when the glass surface temperature is 575°C, and is excellent when the glass surface temperature is 625°C.

Example 8

The general coating procedure described in Example 3 is utilized, including the temperature of 600°C at the surface of the glass bottles. In this example, coatings with a thickness of 200 CTU were prepared, while varying the ratio of the tin compound to the silicon compound in the gas mixture used for forming the coatings. Monobutyl tin trichloride was used in a ratio of  $1 \times 10^{-3}$  moles per 1 mole of air. The tetraethoxy silane concentration was varied. Water vapor was present at a molar ratio to the tin compound + the silicon compound of

11.5, which corresponds with an amount of water vapor of 1.3 - 3.45 moles per 100 moles of air.

The coated bottles were subjected to a 6 hours washing with caustic solution as described in the preceding Examples. The tin compound/silicon compound ratios and the results of the washing tests are given in the Table below.

TABLE		
	molar ratio	result of washing test
10	tin compound/silicon compound	
	0.5 (comparative)	strong haze; coating severely attacked
	0.6	slight haze
15	0.9	no haze (=fully clear)
	1.2	slight haze
	1.5	slight haze
	3.4 (comparative)	haze; coating attacked
	10.1 (comparative)	strong haze; coating severely attacked
20		

Since "no haze" is the most desired result and a "slight haze" is a still acceptable result. it will be clear that the molar ratio of the tin compound to the silicon compound is preferably chosen in the range of 0.6 to 1.5.

CLAIMS

1. Process for producing a protecting coating on a surface of a glass or ceramic article, wherein a stream of an oxygeneous carrier gas containing a thermodecomposable precursor of tin oxide ( $\text{SnO}_2$ ) and a thermodecomposable precursor of silicon oxide ( $\text{SiO}_2$ ) in a molar ratio of the former precursor to the latter between 0.6 and 3.0, said precursors being present in evaporated form, and further containing water vapor in an amount of at least 1 mole per 100 moles of carrier gas, is uniformly impinged onto the surface to be coated, said surface having a temperature which is above the decomposition temperatures of said precursors and amounts to at least  $550^\circ\text{C}$ , to deposit a mixed oxide protecting coating comprising tin oxide and silicon oxide, and the deposition is continued until a coating thickness of between 240 and 1,500 Å is obtained.
2. Process according to claim 1, wherein the molar ratio of the precursor of tin oxide to the precursor of silicon oxide is at most 2.0.
3. Process according to claim 2, wherein the molar ratio of the precursor of tin oxide to the precursor of silicon oxide is at most 1.5.
4. Process according to any of claims 1-3, wherein the carrier gas contains  $0.5 \times 10^{-4}$  -  $2 \times 10^{-2}$  mole precursor of tin oxide per 1 mole of carrier gas.



5. Process according to any of claims 1-4, wherein the carrier gas has a temperature between 100°C and 210°C, preferably between 120°C and 180°C.
- 5 6. Process according to any of claims 1-5, wherein the gas stream impinges on the surface to be coated at a velocity of 1-10 m/s.
7. Process according to any of claims 1-6, wherein the  
10 temperature of the surface to be coated is maintained at a value of at least 570°C during the coating process.
8. Process according to claim 7, wherein the temperature of the surface to be coated is maintained at a value of at least  
15 600°C during the coating process.
9. Process according to any of claims 1-8, wherein the thermodecomposable precursor of tin oxide is selected from monoalkyl tin trichlorides, monoalkyl tin tribromides, dialkyl  
20 tin dichlorides, dialkyl tin dibromides and tin tetrachloride.
10. Process according to claim 9, wherein the thermodecomposable precursor of tin oxide is selected from monomethyl tin trichloride, monobutyl tin trichloride and  
25 dimethyl tin dichloride.
11. Process according to any of claims 1-10, wherein the thermodecomposable precursor of silicon oxide is a compound having the formula  $R_nSiX_{(4-n)}$ , wherein R is an alkyl, an  
30 alkenyl, an alkynyl or an alkoxy group having 1-5 carbon atoms, or a phenyl group; X is a halogen atom or a hydroxy group; and n is a number from 0 to 4.
12. Process according to any of claims 1-11, wherein the  
35 deposition is continued until a coating thickness of between 450 and 900 Å is obtained.

13. Process according to any of claims 1-12, wherein the deposition is carried out by atmospheric-pressure CVD using air as the carrier gas.
- 5 14. Process according to any of claims 1-13, wherein the protecting coating is produced on the outer surface of a glass container intended for repeated use, or on crockery.

## INTERNATIONAL SEARCH REPORT

International Application No

PC1/NL 96/00087

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C17/245

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 13393 (ELF ATOCHEM NORTH AMERICA,INC.) 8 July 1993  see page 1, line 7 - line 12; claims; examples; tables	1-5, 7-11,13, 14
A	see the whole document	6,12
A	--- EP,A,0 485 646 (KIRIN BEER KK) 20 May 1992 see the whole document	1-14
A	--- EP,A,0 309 902 (PPG,INDUSTRIES,INC.) 5 April 1989 see column 7, line 2 - line 20 --- -/-	1,5,6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Harbron, J

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International Application No  
PCT/NL 96/00087

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